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THE CRYSTAL STRUCTURE OF ZINC 8-HYDROXYQUINOLINATE DIHYDRATE

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SUMMARY

The crystal structure of zinc 8-hydroxyquinolinate dihydrate, $Zn(C_8H_7OH)_2 \cdot 2H_2O$ has been determined by single crystal methods. The unit cell is monoclinic with

$$a = 11.28\text{\AA}^\circ \quad b = 5.42\text{\AA}^\circ \quad c = 13.16\text{\AA}^\circ \quad \beta = 106^\circ 18'$$

The space group is $P_{2}1/a$ - $C^5_{\bar{1}}ah$ and there are two molecules per unit cell.

Atomic positions were determined by Fourier projections and were refined by a three-dimensional Fourier electron-density synthesis and by the method of least squares. Structure factors were obtained from visually estimated intensities on Weissenberg photographs taken with Cu K α radiation.

The molecule, with the exception of the water molecules, is essentially planar. Including the water molecules, there is a sort of distorted octahedral arrangement of bonds around the central zinc ion. The Zn-O and Zn-N bond lengths are 2.05\AA° and 2.06\AA° , respectively, while the Zn-CH₃ bond length is 2.27\AA° .

INTRODUCTION

This report is the second in a series from these laboratories dealing with the crystal structure of organic reagents of analytical importance and the complexes they form with metallic ions. The first report (Merritt and Lanterman, 1952) concerned the structure of dimethylglyoxime. Unlike dimethylglyoxime which is quite selective in its action, 8-hydroxyquinoline reacts with a large number of different ions.

Experimental Technique, Unit Cell and Space Group

Single crystals of zinc 8-hydroxyquinolinate dihydrate are quite difficult to prepare. The zinc salt is precipitated from an acetic acid solution by addition of a slight excess of a 5% solution of 8-hydroxyquinoline in 12% acetic acid and subsequent neutralization with dilute ammonium hydroxide. The precipitate consists of very small crystals which give a powder pattern identical with that of powdered single dihydrate crystals. This finely crystalline precipitate is washed thoroughly with hot water to remove any excess 8-hydroxyquinoline and then

is dissolved in pyridine. Water is added to the pyridine solution, kept at about 80°C until a precipitate begins to form. The precipitate is redissolved by adding a little pyridine and the whole solution is cooled slowly, in an oven, to room temperature. Cooling over a period of two or three days yields crystals of usable size, however, most crystals are lamellar twins, twinning plane (001). Only rarely does one find a good single crystal. The crystals are pale yellow and translucent. The refractive indices were determined by the usual immersion methods to be

$$a = 1.650 \pm 0.002 \quad \beta = 1.78 \pm 0.02 \quad \gamma = >1.82$$

Sign of refraction = -

So few well-formed single crystals were available that the orientation of the indicatrix was not thoroughly established; however, $b = \gamma$

The unit cell dimensions were obtained from oscillation photographs and from Weissenberg photographs employing the method of ω separations (Buerger 1942). The results are

$$a = 11.284^\circ \quad b = 5.42A^\circ \quad c = 13.16A^\circ \quad \beta = 106^\circ 18'$$

The density by the flotation method is 1.682 g./cm.⁻³ which gives 1.98, i.e., 2 molecules per unit cell. By an unusual coincidence in this crystal, pointed out by Hughes (1950), there exists a good check on the consistency of the values of a , c and β . On Weissenberg photographs of twinned crystals rotated about the [010] axis, every third layer where $h = 0, 6$ or 12 consists of single spots whereas otherwise the spots are doublets. Only when all of the spots begin to be resolved into $K_{\alpha 1}$ and $K_{\alpha 2}$ doublets are these spots on every third layer resolved into three or four spots. This indicates that the reciprocal lattice moves 20° in going $6a^\circ$ so that using the values of a and c found previously:

$$\cos \beta = \frac{c}{a} = \frac{5.42}{11.284} \quad (1)$$

$$\text{and } \beta = 106^\circ 36' \quad (2)$$

This value of β checks well with that found above.

Complete sets of equi-inclination Weissenberg photographs about the [100] and [010] axis were taken for intensity estimation. The crystals used were roughly 1 mm. long by 0.2 mm. in diameter. No corrections for absorption were made. Copper $K\alpha$ radiation filtered through nickel was employed and relative intensities were estimated visually by comparison with a standard intensity strip prepared by making a series of timed exposures of the (202) reflection. The multiple film technique of Robertson (1943) was employed using four sheets of Eastman No-Screen X-ray film and a factor of 3.7 for the decrease in intensity on passage of the beam through one layer of film. The usual corrections for the Lorentz and polarization factors, the oblique penetration of the film by the X-rays for non-equatorial layer photographs, and the relative time factor of Cox and Shaw (1930) were applied. The zero layer Weissenberg film about [100] was taken as the standard film and by cross calibration all intensities were reduced to this common level. Relative $|F_0|$ values were calculated.

Systematic absences were noted for $h0l$ when h is odd

$0k0$ when k is odd

$h00$ when h is odd

with the single exception that an extremely weak reflection was observed at the

place where (010) should occur. If this is a true reflection then the space group could be P_{2}/a or P/c . The external morphology of the crystal shows a two-fold axis of symmetry which would fix the space group as P_{2}/a . However, it is impossible to pack the required two molecules satisfactorily in the unit cell in this space group with the short b axis existing in this crystal. Therefore it appears certain that the correct space group is $P_{2}/-C\bar{5}ah$ and that the very weak (010) reflection is most probably due to an internal reflection or perhaps to some slight disorder in the [010] direction.

Determination of Atomic Positions

A Patterson projection, Figure 1, upon (010) is sufficiently well resolved to yield a trial structure. Contour lines in Figure 1 are drawn at arbitrary levels of 100, the zero contour being dotted. Crosses represent the ultimate positions of projected vectors between the zinc atom and the other atoms of the same molecule.

Structure factors, F_{hkl} , were calculated for this trial structure. Atomic scattering factors were taken from the Internationales Tabellen with corrections applied to those for zinc due to dispersion of the K electrons (James 1950). Since the zinc atom contributes to all of the 182 terms of this zone, nearly all signs are positive. Actually the signs of 154 terms appeared to be definitely fixed so that they could be included in the first Fourier projection. Three Fourier projections served to refine the x and z parameters. Only a very few of the weaker terms changed sign in the process of refinement. The third Fourier projection on (010) is shown in Figure 2. Contours are drawn at intervals of $1e \text{ \AA}^{-3}$ except near the origin where the contour interval is $5e \text{ \AA}^{-3}$. The one electron contour is dotted and the crosses show the final positions of the projected atomic centers after the structure determination was completed. For comparison purposes the final structure is shown as if projected on (010) in Figure 3.

After each projection a temperature and scale factor was determined by the method of least-squares using the following equation to represent the relationship between $|F_o|$ and $|F_c|$.

$$k|F_o| = |F_c| \exp - B \left(\frac{|F_o|}{|F_c|} \right)^2 \quad (3)$$

The value of $R = \sum |F_o - F_c| / \sum |F_o|$ decreased from 0.81 to 0.18 and 0.164 during the process of these refinements. Centers of peaks were determined by the method of Carpenter and Donohue (1950). After the x and z parameters were established by the projection on (010) an estimate of the tilt of the molecule was made by measuring the bond lengths in the benzene and pyridine rings, in projection, and comparing these lengths with the expected values. It was estimated that the molecule was tilted about 49° around an axis nearly perpendicular to [100] and lying in the (010) plane. From this information the y parameters were estimated and the structure factors for all reflections were calculated. By trial and error it was discovered that better agreement between $|F_o|$ and $|F_c|$ could be obtained if the angle of tilt were increased to 50° . At this point it was decided to carry out the refinement with a three-dimensional Fourier synthesis, since ordinary projections along [100] or [001] would not show many resolved atoms.

Slight corrections were obtained from the three-dimensional density function. It appears that the molecule is tilted about 50.5° around an axis inclined 94° to [100] and also which makes a slight angle of $3 3/4^\circ$ with the (010) plane.

A least-squares refinement of the parameters according to the method of Hughes (1941) completed the structure determination. All of the 1636 reflections within the region investigated were included in this treatment. Only the diagonal terms were calculated and used in solving the normal equations. The final corrections from the least-squares method averaged 0.025 \AA^* per parameter with a

maximum of 0.10\AA° in the z parameter of the C₁ atom. Final parameters for the atoms are given in Table I. The final values of |F_o| and F_c are given in Table II. The final value of B, the exponent in the temperature factor expression, was $2.23 \times 10^{-16} \text{ cm}^2$.

There are 213 unobserved reflections. If those for which F_c is below the minimum observable value for the region of the film in which the reflection should occur are not counted but those for which F_c would indicate the reflection should have been observed are taken at the minimum observable value of F_c, then R turns out to be 0.226. If these 213 reflections are left out altogether R would be 0.219.

The calculations of the Fourier density functions, structure factors and least-squares refinement were carried out with the aid of I.B.M. machines (Donohue and Schomaker, 1949; Shaffer, Schomaker and Pauling, 1946).

TABLE I

Atomic Parameters of Zinc 8-hydroxyquinolinate Dihydrate

Atom	Fraction of Cell Edge		
	x	y	z
C ₁	0.158	0.286	0.194
C ₂	0.204	0.326	0.301
C ₃	0.167	0.175	0.372
C ₄	0.037	0.832	0.396
C ₅	0.951	0.646	0.350
C ₆	0.909	0.623	0.244
C ₇	0.952	0.770	0.178
C ₈	0.41	0.958	0.225
C ₉	0.082	0.978	0.335
O ₁	0.912	0.762	0.076
O ₂	0.156	0.734	0.002
N ₁	0.079	0.104	0.156
Zn	0.000	0.000	0.000

Discussion of Structure

The dimensions of a single asymmetric unit are presented in Figure 3 and Table III. Because of the presence of a heavy atom in the structure the positions of the lighter atoms cannot be fixed as accurately as desired. It seems probable that errors in bond distances between light atoms may be as high as 0.06 to 0.08 \AA judging by the bond lengths in the benzene and pyridine ring and little weight should be placed on the irregularities in the bond lengths in these rings. The lengths of the bonds around the zinc atom, which are the most interesting in this crystal, are undoubtably more precise due to the exact knowledge of the position of the zinc ion and should not be in error by more than about 0.03 to 0.04 \AA .

It would appear that the major distortions in bond angles which results from formation of the five-membered ring are in the angles around the zinc ion and around the nitrogen atom. The Zn - N - C₆ angle has been decreased significantly from the expected angle of 120°.

The arrangement around the zinc atom is that of a distorted octahedron. This is shown schematically in Figure 4. The bond angle of 79.8° between the oxygen, zinc and nitrogen atoms of the main part of the molecule probably represents a sort of compromise due to the rigid structure of the organic chelating molecule and the inability to approach closer to the zinc atom without causing too short bonds and too great a negative charge upon the zinc atom. A somewhat similar distorted octahedral arrangement is found in nickel glycine dihydrate (Stosick, 1945). If the ligands were free to move as necessary then a more regular octahedral structure would be expected such as was observed by Tang and Sturdivant (1952) in manganese chloride-hexamethylene diamine complex.

The zinc atom has a closed third electron shell and therefore the bonding of the six groups must be through use of the 4s, 4p³ and 4d² orbitals. This would be similar to the case of the above mentioned manganese complex where magnetic susceptibility measurements have shown five unpaired electrons. There is undoubtably considerable ionic character in these bonds.

From the normal covalent radii ascribed to oxygen (0.66 \AA) and to nitrogen (0.70 \AA) and the Zn-O₂ and Zn-N bond distances in this crystal, it appears that the octahedral covalent radius of the zinc atom is about 1.38 \AA . Pauling (1945) lists 1.31 \AA as the tetrahedral covalent radius of zinc. The increase of about 0.07 \AA seems reasonable if the unstable 4d orbitals are involved at all.

The water molecules are much less firmly attached to the zinc atom than is the organic molecule as shown by the greater Zn-O₂ distance and confirmed by the fact that the compound loses these water molecules on drying above 135°C. The anhydrous complex is undoubtably tetrahedral since Liu and Bailar (1951) have been able to resolve the anhydrous zinc complex of 8-hydroxyquinoline-5-sulfonic acid into optically active isomers. Mundy (1948) has shown that the copper 8-hydroxy-quinolinate complex exists in two forms, an anhydrous form with space group P₂₁/c and four atoms per unit cell and a dihydrate isomorphous with the zinc complex. According to this observation, there is no reason why the anhydrous form, at least of the copper complex, should not be tetrahedral. It is interesting to note that the resolved compounds of Liu and Bailar are easily racemized on standing in water which might indicate that they pick up two water molecules and revert to the structure shown in this report.

The molecules in zinc 8-hydroxyquinolinate dihydrate show no unusually close approaches. The smallest intermolecular distance is 3.45 \AA between adjacent water molecules. The closest approach of carbon atoms is 3.47 \AA . These distances

eliminate the possibility of hydrogen bonding and indicate that molecular binding in the crystal is mainly through van der Waals forces.

The hydrogen atoms, which altogether contribute 8% of the scattering matter of the unit cell, were neglected entirely in this determination. Inclusion of the hydrogens would probably improve slightly the agreement between observed and calculated structure factors. It is also probable that an anisotropic temperature factor would materially improve the agreement. A root-mean-square displacement of the atoms of 0.17\AA is indicated from the value of B in the temperature factor expression.

The atoms of the 8-hydroxyquinoline molecules and the zinc atom all lie in a plane within the limits of experimental error except perhaps for the oxygen atom, O_1 , which seems to be about 0.10\AA below the least-squares-best plane. If the five-membered ring alone is considered, none of the atoms in this ring are more than 0.05\AA from a plane. The equation of the least-squares-best plane for the whole assymmetric unit in terms of the unit cell vectors is

$$a - 0.3994b - 0.2554c = 0 \quad (4)$$

The average deviation of atoms from this plane is 0.03\AA and the maximum deviation is 0.10\AA for the oxygen atom O_1 .

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TABLE III

Interatomic Distances and Angles in
Zinc 8-Hydroxyquinolinate Dihydrate Crystal

Bond	Distance	Bonds	Angle
Zn-O ₁	2.054°	O ₁ -Zn-N	79.8°
Zn-N	2.06	O ₁ -Zn-O ₂	94.6
Zn-O ₂	2.27	N-Zn-O ₂	92.7
N-C ₁	1.33	Zn-N-C ₈	111.8
C ₁ -C ₂	1.38	N-C ₅ -C ₇	116.1
C ₂ -C ₃	1.40	C ₈ -C ₇ -O ₁	117.4
C ₃ -C ₉	1.42	C ₇ -O ₁ -Zn	114.3
C ₈ -C ₉	1.40	N-C ₁ -C ₂	120.9
C ₈ -N	1.37	C ₁ -C ₂ -C ₃	119.9
C ₄ -C ₉	1.32	C ₂ -C ₃ -C ₉	121.1
C ₄ -C ₅	1.41	C ₃ -C ₉ -C ₈	113.5
C ₅ -C ₆	1.34	C ₉ -C ₈ -N	125.1
C ₆ -C ₇	1.37	C ₈ -N-C ₁	119.0
C ₇ -C ₈	1.44	C ₇ -C ₈ -C ₉	118.8
C ₇ -O ₁	1.29	C ₈ -C ₉ -C ₄	121.0
		C ₉ -C ₄ -C ₅	120.1
		C ₄ -C ₅ -C ₆	120.6
		C ₅ -C ₆ -C ₇	121.6
		C ₆ -C ₇ -C ₈	117.8
		C ₆ -C ₇ -O ₁	124.4
		Zn-N-C ₁	128.9
		C ₃ -C ₉ -C ₄	125.6

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TABLE II
Observed and Calculated Structure Factors

The reflections in the following table are listed in groups with h and k constant in each group. The first column gives the l index, the second gives the calculated structure factor, and the third gives the observed structure factor. All values of structure factors have been multiplied by ten to eliminate decimals.

001

l	F _c	F _o	l	F _c	F _o	l	F _c	F _o
2	-36	57	6	216	221	13	72	85
3	800	920	7	218	219			
4	273	336	8	268	267			
5	767	1005	9	315	345			
6	589	768	10	-22	73			
7	146	129	11	-58	28			
8	279	340	12	100	136			
9	236	320	13	62	97			
10	235	315	14	77	115			
11	271	326	15	49	71			
12	299	375						
13	274	361						
14	150	173						
15	108	133						
16	103	94						
	011							
1	150	112						
2	95	94						
3	264	241						
4	153	127						
5	230	256						
6	168	170						
7	-124	112						
8	-121	60						
9	-11	421						
10	-21	53						
11	-154	126						
12	-18	23						
13	120	60						
14	-31	30						
15	24	25						
16	2.0	<0						
	021							
0	-2d	169						
1	39	51						
2	100	46						
3	209	227						
4	318	336						
5	132	127						

1	Fc	Fo	1	Fc	Fo	1	Fc	Fo	
5	-22	14	1	521	462	2	414	343	
6	74	34	2	256	213	3	583	411	
7	20	6	3	326	306	4	646	566	
	161		4	319	255	5	380	313	
1	168	140	5	118	60	6	375	276	
2	75	76	6	238	212	7	327	257	
3	-2	19	7	247	232	8	163	191	
4	-11	35	8	114	122	9	313	297	
5	-14	10	9	70	56	10	190	166	
6	27	23	10	11	<25	11	-56	30	
7	30	39	11	-29	26	12	50	65	
8	5	25	12	10	<23	13	160	135	
	200		13	20	<21	14	149	113	
			14	14	<18	15	124	106	
			15	28	<12	16	82	60	
				211			231		
0	1111	1156							
1	145	136	1	604	443	0	12	27	
2	478	543	2	-639	510	1	-84	58	
3	270	241	3	-224	136	2	-219	145	
4	357	443	4	-263	260	3	-171	143	
5	720	832	5	-208	138	4	-67	32	
6	195	269	6	52	71	5	-30	11	
7	-39	<19	7	-297	227	6	-90	83	
8	108	2d4	8	-268	234	7	-269	202	
9	160	181	9	-295	214	8	-264	170	
10	-17	34	10	-209	179	9	21	18	
11	-35	50	11	82	56	10	142	101	
12	266	271	12	-17	25	11	-23	37	
13	153	182	13	10	30	12	-53	27	
14	54	120	14	4	<21	13	-56	35	
15	91	99	15	-90	46		231		
	201		16	11	30				
				221					
1	826	618					1	-27	42
2	-80	78	0	470	405	2	-88	76	
3	112	181	1	227	239	3	-6	39	
4	-111	110	2	84	83	4	168	122	
5	106	212	3	314	313	5	173	115	
6	282	310	4	294	253	6	148	83	
7	233	313	5	289	276	7	149	101	
8	380	427	6	340	313	8	132	78	
9	233	264	7	212	181	9	141	83	
10	121	244	8	343	290	10	69	64	
11	271	317	9	318	313	11	-3	423	
12	273	317	10	172	177	12	33	423	
13	102	169	11	233	209	13	37	419	
14	100	154	12	113	113	14	6	416	
15	130	182	13	69	101	15	1	411	
16	22	60	14	126	124		241		
	211			221					
0	-597	513	1	465	352	0	194	170	
						1	198	172	
						2	291	239	

1	Fe	Fo	1	Fe	Fo	1	Fe	Fo
3	304	242		261		13	222	225
4	182	136	0	88	64	14	124	150
5	87	89	1	12	14	15	139	158
6	91	73	2	179	129	16	65	76
7	103	94	3	1d4	74		321	
8	132	103	4	39	30	0	55	62
9	46	42	5	125	61	1	-165	170
10	24	34	6	53	37	2	-123	71
11	93	71	7	81	76	3	222	195
12	28	35		261		4	-16	118
	241					5	103	92
1	247	181	1	124	103	6	-19	57
2	124	372	2	100	90	7	-270	212
3	145	53	3	190	135	8	120	170
4	186	175	4	142	135	9	143	115
5	136	127	5	146	104	10	-24	123
6	182	159	6	111	80	11	-1	123
7	99	76	7	53	62	12	-16	27
8	-45	19	8	109	67	13	-26	16
9	191	136		311		14	-3	11
10	257	191					321	
11	105	97						
12	131	110	0	577	565	1	167	145
13	114	61	1	-7	46	2	9	39
	251		2	350	322	3	-77	44
0	89	50	3	355	304	4	-167	168
1	-41	<25	4	427	396	5	-61	27
2	28	67	5	440	437	6	259	260
3	113	51	6	185	211	7	35	51
4	4	<23	7	236	237	8	-99	76
5	70	50	8	213	244	9	-61	55
6	36	65	9	115	179	10	15	<23
7	58	44	10	144	165	11	51	41
8	62	41	11	162	172	12	-72	41
9	54	32	12	170	179	13	73	60
10	-25	<12	13	103	104	14	75	23
	251		14	59	76	15	-57	37
				311		16	14	<11
1	-42	34		999	639		331	
2	181	122	2	190	115			
3	-166	69	3	201	179	0	200	166
4	-108	67	4	511	478	1	256	200
5	3	<23	5	279	260	2	200	179
6	-66	23	6	310	297	3	264	266
7	20	<23	7	346	306	4	145	156
8	-150	99	8	172	166	5	172	166
9	-133	65	9	347	349	6	139	110
10	40	<16	10	355	352	7	-11	19
11	-4	18	11	3	46	8	304	260
			12	66	120	9	210	163

1	F ₀	F ₀	1	F ₀	F ₀	1	F ₀	F ₀
10	-12	9		351		5	278	352
11	134	136	0	232	193	6	257	382
12	49	37	1	224	191	7	270	375
13	66	85	2	231	204	8	76	166
	331		3	113	104	9	57	142
1	138	127	4	104	96	10	15	50
2	339	241	5	168	154	11	59	117
3	284	207	6	156	120	12	145	166
4	176	156	7	121	97	13	39	42
5	226	223	8	74	97	14	72	61
6	226	191	9	121	154		401	
7	124	127		351		1	-181	304
8	180	163				2	220	289
9	167	143	1	140	149	3	275	289
10	43	97	2	-8	30	4	38	35
11	134	152	3	135	140	5	179	234
12	123	97	4	254	246	6	108	147
13	93	110	5	175	177	7	238	331
14	107	110	6	164	161	8	302	375
15	40	37	7	149	104	9	273	343
	341		8	25	21	10	434	563
			9	79	80	11	56	140
0	56	25	10	213	145	12	-93	9
1	81	69	11	146	110	13	136	188
2	19	19		361		14	43	76
3	-89	67				15	112	168
4	88	73	0	-17	18	16	83	120
5	-3	18	1	4	34		411	
6	40	23	2	-27	16			
7	41	39	3	-10	16	0	-242	168
8	-97	64	4	-16	14	1	-321	276
9	-6	21	5	-5	12	2	-238	154
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11	6	14		361		4	-267	234
12	5	15				5	-160	136
	341		1	24	19	6	16	76
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1	17	<23	3	34	19	8	22	42
2	121	76	4	29	16	9	-26	30
3	-167	142	5	-22	15	10	79	74
4	-63	62	6	-17	16	11	-32	9
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6	-35	41	8	-3	12	13	-19	7
7	113	46		401		14	-59	28
8	-6	46					411	
9	-115	87						
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11	11	<21	1	293	365	2	103	60
12	1	<10	2	248	294	3	-55	19
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4	384	391	8	-55	55	10	-15	12
5	342	349	9	-54	50			
6	-4	9	10	28	23			
7	120	152	11	-12	30			
8	294	271	12	-62	53			
9	119	136	13	16	21			
10	71	106	14	40	49			
11	150	135	15	-6	46			
12	105	106	16	-17	41			
13	70	63						
				531				
	511							
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2	331	292	1	299	257			
3	246	195	2	182	179			
4	381	317	3	186	205			
5	350	324	4	186	189			
6	157	142	5	67	127			
7	199	179	6	181	191			
8	280	271	7	194	189			
9	253	262	8	88	108			
10	281	260	9	78	80			
11	111	133	10	141	112			
12	73	76	11	84	76			
13	164	152		531				
14	69	97						
15	127	140						
16	128	120						
	521							
0	164	184						
1	21	74						
2	54	112						
3	112	124						
4	-91	30						
5	83	64						
6	-87	87						
7	-93	37						
8	169	143						
9	50	30						
10	11	19						
11	-18	21						
12	65	62						
	521							
1	341	263	0	-30	23			
2	53	18	1	42	25			
3	-371	315	2	-27	57			
4	-23	41	3	-92	74			
5	-56	76	4	46	27			
6	-13	9	5	-3	21			
			6	27	32			
			7	-79	50			
			8	-102	42			

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3	-31	50	9	83	76	15	53	89
4	-41	50	10	50	48	16	21	34
5	-45	23	11	41	14			
6	2	14						
7	-9	19						
	-18							
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1	164	195	2	-66	48	1	124	142
2	135	227	3	24	25	2	118	115
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4	381	439	5	-124	104	4	38	46
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6	286	414	7	129	81	6	36	32
7	292	396	8	108	80	7	64	50
8	343	370	9	116	81	8	32	55
9	186	269	10	111	60	9	6	6
10	181	246	11	117	108	10	551	
11	216	234	12	55	25	11		
12	106	135	13	40	23	12		
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			15	15	19	14		
			16	621	14	15		
0	601							
1	337	430	0	81	84			
2	382	455	1	185	173			
3	419	434	2	161	154			
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6	357	412	5	53	69			
7	201	292	6	-92	53			
8	411	501	7	41	92			
9	198	306	8	113	112			
10	529	581	9	30	35			
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12	-239	214	11	91	104			
13	78	106	12	41	37			
14	219	179						
15	118	136						
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	611							
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1	-257	214	2	394	362			
2	22	19	3	25	37			
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4	-94	64	5	6	65			
5	-14	50	6	51	96			
6	-293	246	7	169	181			
7	-36	19	8	14	46			
			9	93	90			
			10	117	110			
			11	73	119			
			12	179	170			

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6	232	221	4	258	289	11	49	42
7	230	193	5	147	133	12	20	25
8	136	112	6	-2	14	13	31	19
9	196	124	7	180	209	14	45	34
10	148	124	8	188	191	15	-11	14
11	75	87	9	91	101			
12	116	74	10	110	115			
13	53	53	11	63	57			
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	651					1	274	212
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	651			197	191		731	
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4	-35	39		14	115	3	-143	58
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9	14	16			1	8	133	143
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	53	50			85	11	153	112
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0	120	145		4	-139	13	93	90
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				11	34	1	60	62
1	126	161			<16	2	-5	23
2	61	85			42	3	117	21
3	43	34			721	4	53	48
4	4	32				5	31	14
5	66	76				6	-27	16
6	24	21				7	-19	16
						8	86	78
	711						741	
0	167	159						27
				7	5	1	-12	
				8	<23			

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4	-14	27	9	124	253	2	163	168
5	-48	53	10	131	169	3	274	266
6	-57	55		501		4	169	147
7	5	23		323	407	5	118	127
8	19	21		405	524	6	176	149
9	-28	21		246	377	7	110	92
10	-7	9		276	405	8	53	44
11	0	10		444	570	9	14	16
12	-26	34		333	393	10	61	35
13	-46	11		7	50			
	751			135	244			
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2	120	104		198	246			
3	52	46		25	27			
4	52	44		67	67			
5	26	27		125	152			
	751			84	129			
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2	90	90						
3	122	90		0	172			
4	59	32		1	119	147		
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0	12	23						
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3	36	11		3	-165	145		
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				6	49	27		
				7	-135	110		
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1	133	251		10	-45	25		
2	262	379		11	123	92		
3	109	230		12	-153	115		
4	307	419		13	-240	131		
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6	-103	50		15	-30	30		

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12	39	19	6	-33	34	4	215	248
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14	67	37	8	-18	23	6	15	81
			9	113	65	7	61	81
			10	-25	23	8	46	81
			11	-8	21	9	27	65
0	911		12	34	19	10	66	76
1	107	120	13	-66	41	11	39	57
2	217	235	14	-2	11	12	44	76
3	234	207	15	8	15	13	161	173
4	159	147				14	90	92
5	128	120				15	35	73
6	50	50						
7	125	110						
8	143	120						
9	73	97						
	127	104						
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4	171	136						
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6	256	204						
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9	102	124						
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9	-1	7						
	921							
1	4	23						
2	-117	73						
3	137	106						

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2	138	156	4	-13	23	10	94	65
3	168	168	5	153	127	11	64	35
4	89	94	6	285	214		1201	
5	44	32	7	92	103			
6	314	266	8	78	76			
7	339	204	9	85	74			
8	165	156	10	70	71	0	168	235
9	165	133	11	181	136	1	178	253
10	153	127	12	116	99	2	180	221
11	151	140	13	43	25	3	82	122
12	266	235		1121		4	79	69
13	174	154					1201	
14	-9	<11	0	82	65	1	183	212
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			2	-40	19	3	139	182
			3	47	46	4	118	122
			4	45	41	5	73	53
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1	19	19	6	-15	7	7	93	119
2	2	<21		1121		8	154	168
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5	-56	57				4	52	58
6	-69	60						
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	1111		1	55	55	5	99	69
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0	131	133	4	53	35	8	13	<19
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2	116	110				10	62	18
3	163	152				11	-34	23
4	55	46	1	107	92	12	-25	19
5	0	25	2	70	81			
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	1111		4	158	170			
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1	72	80	6	53	50	1	32	39
2	198	165	7	134	131	2	25	48
			8	96	73	3	89	92

1 Fe Fo
4 27 <7

1221

1 19 42
2 82 94
3 120 133
4 43 69
5 89 126
6 193 251
7 154 177
8 36 55
9 45 67
10 51 60
11 54 58

1 Fe Fo
3 -52 <16
4 -15 19
5 -22 19
6 -42 <16
7 27 14
8 -70 58
9 -21 12
10 15 <7

1401

1 63 124
2 114 131
3 35 48
4 -125 127
5 205 241
6 223 200
7 35 64

0 11 16
1 23 39

1411

1 -46 16
2 7 <12
3 20 <12
4 -88 67
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1231

1 -40 35
2 -78 85
3 -28 87
4 -42 60
5 -48 23
6 -50 <16
7 -55 16
8 -22 14
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1311

0 102 97
1 39 34
2 91 92

1321

1 112 119
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1321

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2 5 16

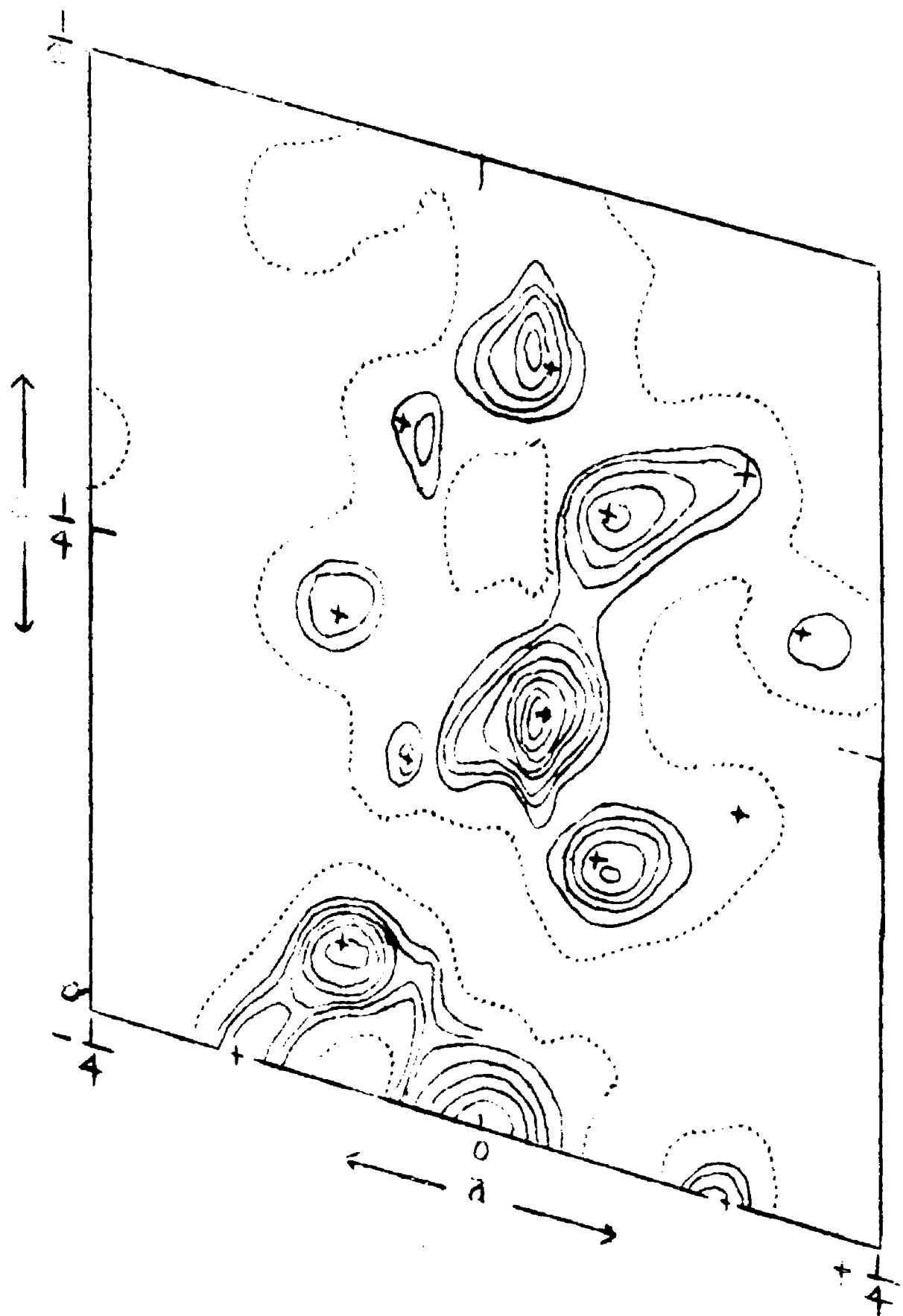


Figure 1. Patterson Projection of Zinc 8-Hydroxyquinolinate Dihydrate Upon (010). Compare With Figures 2 and 3. Crosses Indicate Final Positions of Atom Centers. Contour lines at arbitrary intervals, zero contour dotted, contours around origin at $4x$ value of others.

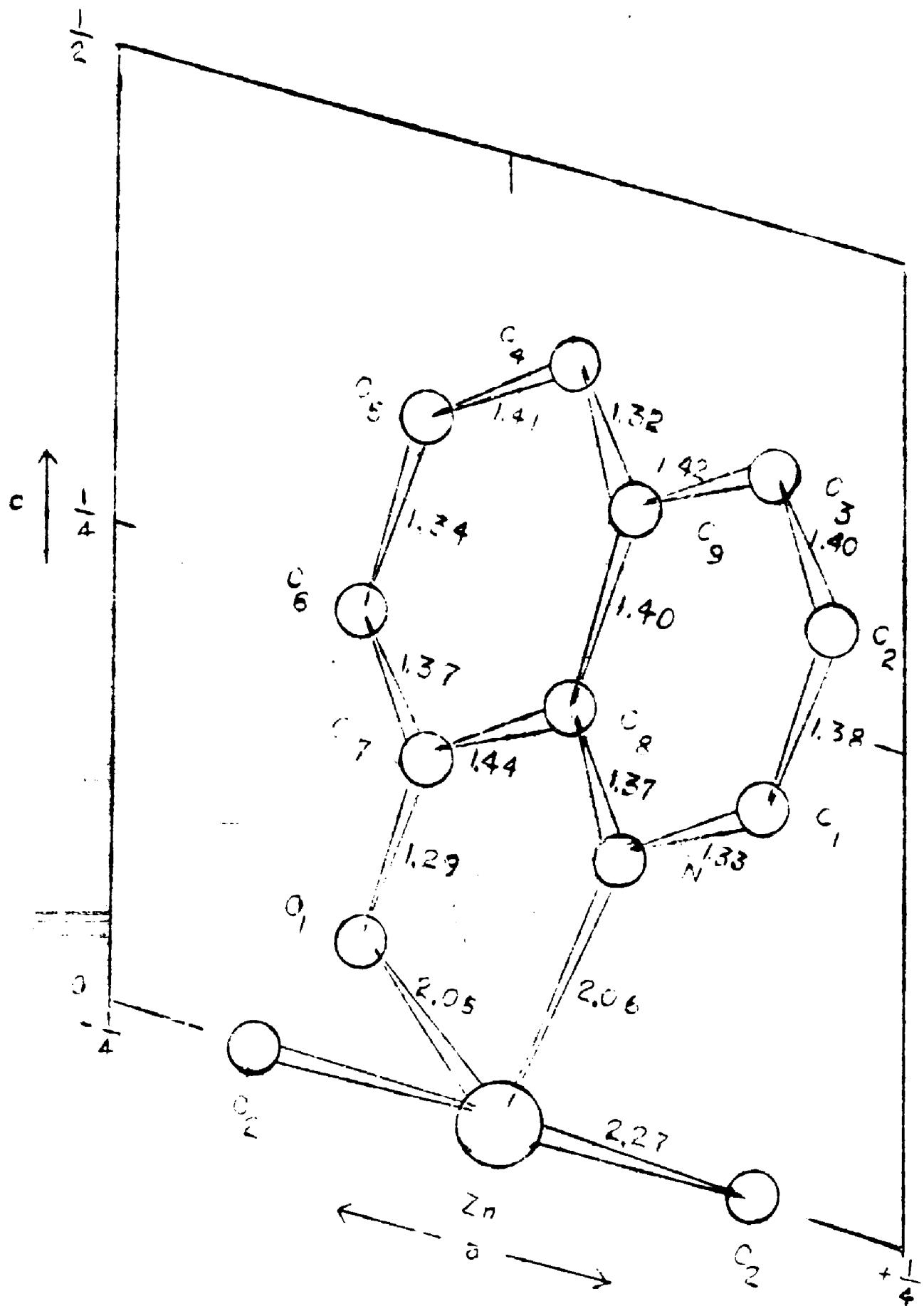


Figure 3. Structure of Zinc β -Hydroxyquinolinate Dihydrate as Seen Projected upon (010). Actual Interatomic Distances Indicated in Angstrom Units.

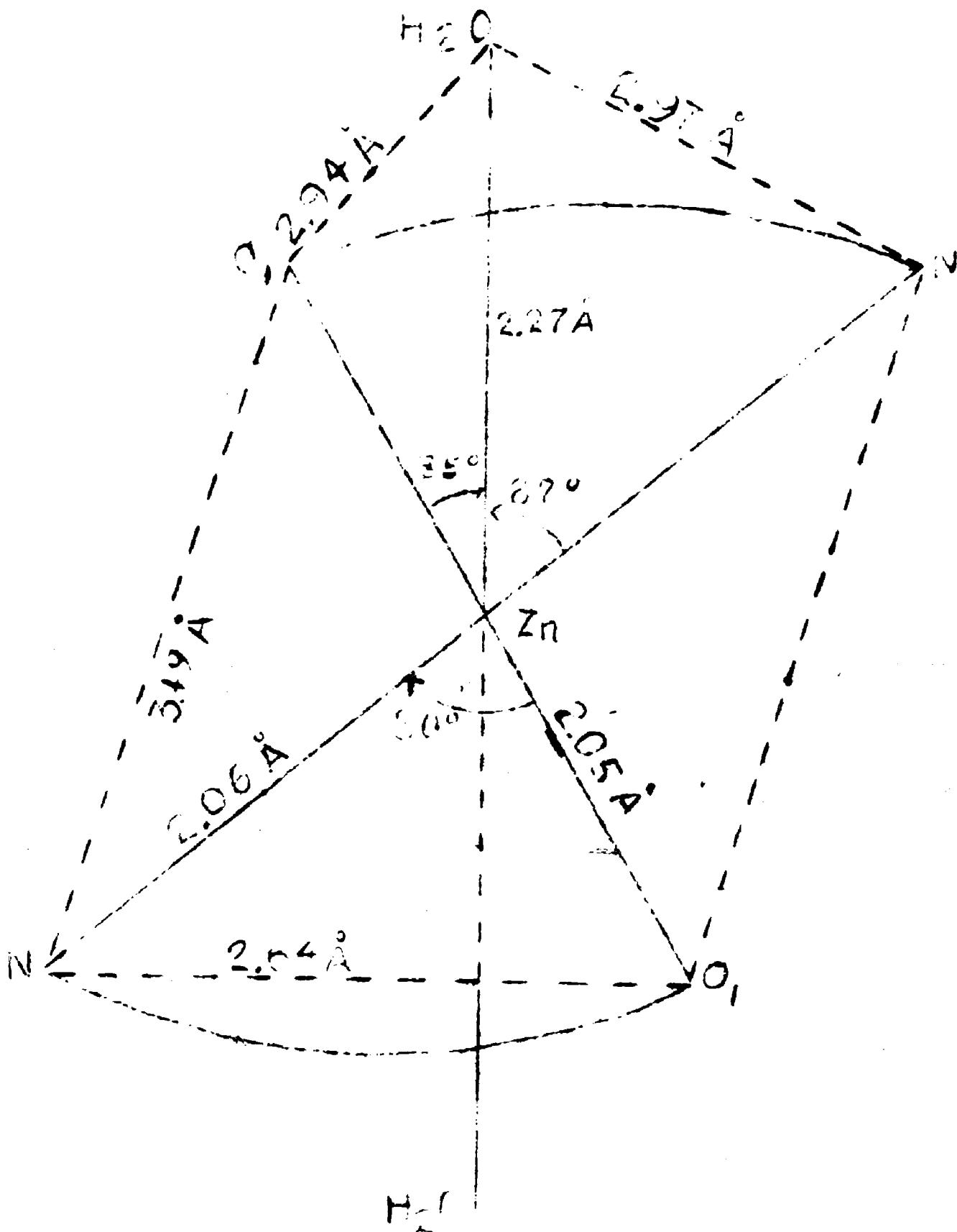


Figure 4. Schematic Representation of Bonds Around Central Zinc Atom in Zinc 8-Hydroxyquinolinate Dihydrate.